MEASUREMENT OF DIFFUSIVITY OF Cu^{64} IN MILD STEEL BY THIN LAYER TRACER TECHNIQUE

by

SAIBAL GANGULY

B. S. (Met. Eng.) Indian Institute of Technology,
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A E Hostetter

Major Professor

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I. INTRODUCTION

The solid state diffusion of one metal into another was realized in the latter part of the eighteenth century. The scientific basis behind the process of diffusion progressed very slowly, even though a substantial attention was drawn towards it. This was so mainly because of non-ideal behaviour of solid solutions. At the present, the concept of diffusion has been clarified to a large extent for binary solutions. For ternary and higher component systems, the behaviours observed have not been understood very well. This is due to the necessity of a large amount of data needed to connect up a theoretical basis. Most of the diffusivity measurements have been done on pure binary solutions. The effects of impurities are not very well understood, though in practice we do not generally come across a system composed of pure metals. This makes it difficult to use diffusion data in practice.

The aim of this work is to study the diffusivity of Cu^{64} in mild steel in the temperature range 600°c. to 940°c. so as to find out the effect of phase changes in mild steel on the process of diffusion.

Copper is used in various utensils and other decorative articles. The ductility of copper many times comes as a disadvantage even though it is necessary to use it because of its good conductivity. One of such cases is the commutator of electric motors and generators. Here copper

strips are brazed on steel to use the strength of steel and the conductivity of copper. Brazing is a costly and slow process. To avoid this, attempts have been made to make inertia weld between copper and steel. In all these cases the diffusivity of copper in steel plays an important role to obtain better bondage in minimum effort.

II. REVIEW OF LITERATURE

Before introduction of artificial isotopes, measurement of diffusivity was a long and tedious process. The use of tracers was introduced in this field by Grosh and Hersy (12, 13) in 1920. They measured the self-diffusion of molten lead by natural occurring isotope. With the introduction of artificial isotopes, the use of tracer technique grew up rapidly. In the period of 1937 to 1940, McKay (27) measured the self-diffusion of gold. Mair and others (26) measured that of copper, followed by Day and others (10) on zinc and Johnson (18) on silver. Stockley and Nix (42) in 1939 introduced the absorption technique. Later on, more methods were introduced, which will be discussed later. During 1955, Zhoukhovitzky and Kryukov (22) introduced the thin layer method and in 1952, Geodakyan and Zhoukhovitzky (50) developed the thick layer technique. These two methods avoided the absorption characteristics and were sucessfully used.

Recently, Kirner (20) investigated the diffusion in Mo-Pt couple. The diffusion followed a $t^{\frac{1}{2}}$ relation. The study was done mainly to examine the formation of η phase which decomposes at 1400°c. Ballufi (3) discussed the diffusion behaviour of Fe, Co, Ni, in Al at 350°c. to 630°c. He attributed the unusual behaviour to dominance of dislocation short circuiting. Costas (9) measured the diffusivity of Be in Al to be 4.5 exp (-33.3/RT). Keys and Duttan (19)

showed that diffusion of Ag in single crystal of Bi and Te is anisotropic and perpendicular to the cleavage plani. Rothy (38) attributed the change to self-diffusivity of Fe at Curie temperature to the frequency factor rather than activation energy for formation of vacancy in ferromagnetic phase. Ichi, Cohen and Averbach (17) used residual activity technique and claimed that diffusion along dislocation line was the controlling factor due to low solubility. Peterson and More (30) suggested a co-related vacancy mechanish for diffusion of Fe^{59} and Cr^{51} in -uranium. Agarwala and others (1) attributed the low frequency factor and activation energy to the low solubility. They used the residual activity technique. Shyris and Tomizuke (42) proposed an anomalous diffusion rate of Zn^{65} in Cu for a small penetration. Shaw, Jones and Hazelby (41) measured the diffusivity of Zn in Al-Antimonide and showed that it follows Fick's law up to a concentration of $8x10^{19}$ atoms/c.c., below which the relation was Arrhenius type with $Q = 1.93 \pm 0.04$ev. and $D_0 = 0.33 \pm 0.15$cm /Sec. Hirano and others (16) attributed the large frequency factor for diffusion of Fe group in Ag to extremely small solid solubility limits. Lundy and Fedirer (24) proposed a graphical method to separate grain boundary and lattice diffusion. Lundy (25) showed that diffusion of Zr^{95} and Nb^{95} in B.C.C. Zr does not follow the Arrhenius relation. Murake and others (31a) attributed the bimodal nature of diffusion of Cr in Ni to the rapid drop of solid solubility. Krishtal and Mokrov (21) discussed the

diffusion mechanism of iron alloys with body-centered cubic lattice. According to them not all vacancies were absorbed by dislocations. In saturated regions, they gathered together and after reaching a critical volume, formed roughly spherical pores. The results indicated that the vacancy mechanism of diffusion was dominant in the alloy studied. Moore (30) co-related the diffusion data in face-centered cubic metals as a function of atomic volume. He proposed a relation of

$$Q = b - a \log v \qquad (1.1)$$

where v is the atomic volume, a and b are constants.

Cohoon and Youdelis (7) measured the diffusion of Cu in Ag rich Cu alloys. Condit and Beshers (8) developed a theoretical relation, considering jumps between tetrahedral and octahedral interstices for body-centered cubic lattice. A collection of diffusion data obtained till 1955 is presented by Seith (40).

III. THE CONCEPT OF DIFFUSION

1. Theory

By analogy to Fourrier's concept of heat conductivity the law governing the diffusion process was proposed by Fick. The law is valid for ideal substances and can be stated as

$$M = -q\ D\ \frac{dc}{dx} \tag{3.1}$$

Where M is the quantity of substance transferred through a cross-section q per unit time; $\frac{dc}{dx}$ is the concentration gradient, and x is the path coordinate. The term D is a constant and is called diffusivity or diffusion co-efficient. The equation (3.1) is known as Fick's first law.

It is difficult to arrange an experiment which can use this law to determine D, as it is not possible to keep the concentration gradient constant, and measurement of amount of solute diffusing is difficult. The change in concentration with time is easier to determine and to facilitate the determination of diffusivity from such a measurement, another relation was derived which is known as Fick's second law.

If we consider a volume $q\Delta x$ at a point x within the diffusion zone, then the quantity (Δmx) which flows into the unit volume in a direction x through the cross-section q in time Δt is

$$\Delta m_x = D \left(\frac{\partial c}{\partial x}\right)_x q \, \Delta t \tag{3.2}$$

The quantity of solute moving out of this volume from a point $x+\Delta x$ in time Δt amounts to

$$\Delta m_{x+\ x} = -D\left(\frac{\partial c}{\partial x}\right)_{x+\ x} q\Delta t = -D\left[\left(\frac{\partial c}{\partial x}\right)_x - \frac{\partial^2 c}{\partial x^2}\Delta x\right] q\Delta t \tag{3.3}$$

so the amount of solute remaining in volume q x in time t is

$$\Delta m_{x+\ x} - \Delta m_x = D \frac{2_c}{x^2} \Delta x q \Delta t \tag{3.4}$$

By the definition of concentration (amount per unit volume) the equation (3.4) yields to Fick's second law as

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{3.5}$$

For a successful application of this defferential equation, to obtain the value of D, it is necessary to have its solution. Under certain achievable limiting conditions, it is possible to have solution of equation (3.5) in different forms. Some of these are discussed below.

One way of getting the solution is by Boltzman expression $\lambda(c) = x/\sqrt{t}$ where $\lambda(c)$ is some function of concentration c. Fick's second law then reduces to

$$\frac{\partial c}{\partial t} = \frac{\partial c}{\partial \lambda} \cdot \frac{\partial \lambda}{\partial t} = - \frac{\partial c}{\partial \lambda} \frac{x}{2t^{3/2}} \tag{3.5a}$$

$$D \frac{\partial^2 c}{\partial x^2} = D \frac{d^2 c}{d\lambda^2} \left(\frac{\partial \lambda}{\partial x}\right)^2 = D \frac{\partial^2 c}{\partial \lambda^2} \cdot \frac{1}{t} \tag{3.5b}$$

equating (3.5a) and (3.5b) we get

$$\frac{dc}{d\lambda} = - 2D \frac{d^2 c}{d\lambda^2} \tag{3.6}$$

The solution of this equation (3.6) is

$$C = \frac{C_2+C_1}{2} - \frac{C_2-C_1}{2} \psi\left(\frac{x}{2\sqrt{Dt}}\right) \tag{3.7}$$

Where C_1 and C_2 are concentrations on two sides of a diffusion couple and

$$\psi\left(\frac{x}{2\sqrt{Dt}}\right) = \frac{2}{\sqrt{\pi}} \int_0^{x/2\sqrt{Dt}} e^{-\xi^2} \, d\xi \tag{3.7a}$$

where

$$\xi = \frac{\lambda}{2\sqrt{D}} \tag{3.7b}$$

Another form of solution can be obtained by the method of separation of variables. Let us assume that the variables x and t are separable and

$$C = X(x)\, T(t) \tag{3.8a}$$

where X(x) and T(t) are functions of x and t respectively. Fick's second law then reduces to

$$X \frac{dT}{dt} = DT \frac{d^2X}{dx^2} \tag{3.8b}$$

which may be written as

$$\frac{1}{T} \frac{dT}{dt} = \frac{D}{X} \frac{d^2X}{dx^2} \tag{3.8c}$$

Since the left hand side of equation (3.8c) depends only upon t, and the right hand side depends only upon x, so both sides must equal to the same constant. This constant can be taken for convenience as $- \lambda^2 D$. Thus, from equation (3.8c) we get two ordinary differential equations

$$\frac{1}{T} \frac{dT}{dt} = - \lambda^2 D \tag{3.8d}$$

$$\frac{1}{X} \frac{d^2X}{dx^2} = - \lambda^2 \tag{3.8e}$$

The solutions of (3.8d) and (3.8e) are respectively

$$T = e^{- \lambda^2 Dt} \tag{3.8f}$$

$$X = A \text{ Sin } \lambda x + B \text{ Cos } \lambda x \tag{3.8g}$$

where A and B are constants.

From equation (3.8a) we get

$$C = (A \text{ Sin } \lambda x + B \cos \lambda x) \, e^{- \lambda^2 Dt} \tag{3.8h}$$

Since Fick's second law is a linear differential equation, so the most general solution is given by

$$C = \sum_{m=1}^{\infty} (Am \, Sin \, \lambda_m x + Bm \, Cos \, \lambda_m x) \, e^{-\lambda_m^2 Dt} \qquad (3.8)$$

The third convenient way to obtain a solution of Fick's second law is by using Laplace's transform. Laplace's transform $\bar{f}(P)$ is defined as

$$\bar{f}(P) = \int_0^{\infty} e^{-Pt} f(t)dt \qquad (3.9a)$$

where P is a number sufficiently large to make the integral converge.

Multiplying equation (3.5) by e^{-Pt} on both sides and then integrating with respect to t from 0 to we get

$$\int_0^{\infty} e^{-Pt} \frac{\partial^2 C}{\partial x^2} dt - \frac{1}{D} \int_0^{\infty} e^{-Pt} \frac{\partial c}{\partial t} dt = 0 \qquad (3.9b)$$

assuming that the orders of differential and integral can be interchanged, which is true for these functions, we get

$$\int_0^{\infty} e^{-Pt} \frac{\partial^2 c}{\partial x^2} dt = \frac{\partial 2}{\partial x^2}\left(\int_0^{\infty} c \, e^{-Pt} \, dt \right) = \frac{\partial^2 \bar{c}}{\partial x^2} \qquad (3.9c)$$

where $\bar{c}$ is the Laplace transform of C.

Also, integrating by parts

$$\int_0^{\infty} e^{-Pt} \frac{\partial c}{\partial t} dt = \left| c \, e^{-Pt} \right|_0^{\infty} + P \int_0^{\infty} c \, e^{-Pt} \, dt = P\bar{c} \qquad (3.9d)$$

if initially C = 0, at x > 0 and t = 0 which is a very usual case.

Fick's second law (3.5) then reduces to

$$D \frac{d^2\bar{c}}{dx^2} = P\bar{c} \qquad (3.9e)$$

whose solution is

$$c = Ae^{-\sqrt{\frac{P}{D}}\, x} + Be^{\sqrt{\frac{P}{D}}\, x} \qquad (3.9)$$

The constants can be evaluated from boundary conditions and the real solution can be found from the table of Laplace transform.

Thermodynamic concept of diffusion plays a major role in explaining the behaviour of diffusion process. In ideal and non-ideal solutions, it is necessary to have a thermodynamic concept of diffusion process.

Let us consider a diffusion couple A-B where B is the solute. Let the concentration gradient be-dc/dx even in an atomic scale. Then the concentration difference between two adjacent atomic planes of lattice spacing a is -a(dc/dx). Let τ be the mean time of stay of an atom in lattice site. The average frequency of jump then is $1/\tau$. Let there be n number of places to which an atom can jump. Out of these n possible jumps; once an atom takes one, it is transferred to next plane. The average frequency with which an atom can

move from one plane to the other is $1/n\tau$. The number of these atoms that will jump per second from one plane to the other equals the total number of atoms in the former plane multiplied by the frequency. The number of solute atoms in former plane equals the number of solute atoms per unit volume (i.e., the concentration c) times the volume of the atom in the plane. So the flux of solute atoms going from one plane to other becomes

$$J_{X \rightarrow y} = - \frac{1}{n\tau} (caq) \qquad (3.10a)$$

where $J_{X \rightarrow y}$ is the flux from X to Y plane.

The concentration at Y plane may be written as

$$C_Y = c + a \frac{dc}{dx} \qquad (3.10b)$$

Therefore

$$J_{Y \rightarrow X} = c+a \frac{dc}{dx} \frac{aq}{nt}$$

where $J_{Y \rightarrow X}$ is the solute flux from Y to X plane.

The net flux (J) then is

$$J = J_{X \rightarrow Y} - J_{Y \rightarrow X} = - \frac{aq}{n\tau} C + \left[c+a \frac{dc}{dx}\right] \frac{aq}{n\tau}$$

or,

$$J = - \frac{a^2 q}{n\tau} \frac{dc}{dx} \qquad (3.10c)$$

Comparing equation (3.10c) to equation (3.1) we get

$$D = \frac{a^2}{n\tau} \tag{3.10}$$

The value of n is dependent on type of atomic arrangement of metals and it can be shown (40) that

$$D_{cubic} = \frac{a^2}{6\tau} \tag{3.11}$$

$$D_{F.C.C.} = \frac{a^2}{12\tau} \tag{3.12}$$

$$D_{B.C.C.} = \frac{a^2}{8\tau} \tag{3.13}$$

It is known (35a) that the number of jumps (r_a) made by one atom in a pure metal crystal per second is related to the enthalpy by the equation

$$r_a = A\, e^{-(Q_m + Q_t)/RT} \tag{3.14a}$$

where

Q_f = Work or enthalpy to form a mole of vacancies

Q_m = Minimum energy required to move a mole of atom into vacancies

A = Product of lattice coordinate number (z) and lattice vibration frequency (ν)

and

$$r_a = \frac{1}{\tau} = Z\nu e^{-(Q_m + Q_f)/RT} \tag{3.14}$$

If we take entropy change into account then Q_m and Q_f can be replaced by free energies F_m and F_f respectively, and we get

$$\frac{1}{\tau} = Z \nu e^{-(\Delta F_m + \Delta F_f)/RT} \tag{3.15}$$

Hence in general,

$$D = \frac{a^2}{n\tau} = \frac{Z\nu a^2}{n} e^{-(\Delta F_m + \Delta F_f)/RT} \tag{3.16}$$

or

$$D = \frac{Z\nu a^2}{n} e^{(\Delta S_m + \Delta S_f)/R} e^{-(Q_m+Q_f)/RT} \tag{3.17}$$

Thus in general diffusion follows Arrhenius relation

$$D = D_0 e^{-Q/RT} \tag{3.18}$$

in which

$$D_0 = \frac{Z \nu a^2}{n} e^{(\Delta S_m + \Delta S_f)/R} \tag{3.18a}$$

and

$$Q = Q_m + Q_f \tag{3.18b}$$

The quantity D_0 is commonly called frequency factor and Q is known as the activation energy and S_m & S_f designates entropy change due to strain produced in the lattice for removing and putting in an atom respectively.

In case of using radioactive tracer to measure diffusivity, the diffusion co-efficient is generally designated by D*.

The jump rates are going to be different due to the differences in mass of natural atom and isotopes. If $1/\tau^*$ is jump rate of an isotope of mass m* then

$$\frac{1}{\tau^*} = \sqrt{\frac{m}{m^*}}\ \frac{1}{\tau} \tag{3.19}$$

as difference between mass of an isotope and natural element is very little (i.e., $m \approx m^*$.) We get from equation (3.19)

$$\tau = \tau^* \tag{3.20}$$

and consequently from equation (3.10)

$$D = D^*$$

In chemical diffusion Darken (35a) has shown that D and D* is related as

$$D_A = D_A^* \left(1+N_A \frac{\partial \ln \gamma_A}{\partial N_A}\right) \tag{3.21}$$

where

γ_A = activity of component A

N_A = atom fraction of A

The term in parenthesis of equation (3.21) is known as the thermodynamic fraction. The value of $N_A \partial \ln \gamma_A / \partial N_A$ is very small and can be neglected. This gives

$$D = D^*$$

2. Determination of Diffusivity

The theoretical basis behind determination of diffusivity has been discussed previously. Some practical manipulation is necessary for measurement of diffusivity. The different methods can be classified in three divisions.

(i) Metallographic and chemical methods

(ii) Physical methods

(iii) Tracer methods

(i) Metallographic and chemical methods

In determination of diffusivity of carbon in iron Tamman and Schonert (44) had cut a longitudinal piece from a diffusion couple. They looked at the section through a microscope and found the distance to which carbon had moved in iron. It was shown that

$$\bar{x}^2 = 2Dt \qquad (3.22)$$

where x was the average depth of penetration. Thus D was calculated.

To determine the diffusivity of copper in aluminum, Brick and Phillips (6) used the precipitation technique. The solubility of copper in aluminum decreases with temperature so they cooled a copper-aluminum couple to a known temperature after diffusion anneal. The composition of the plane from which precipitation occurred was read from phase

diagram, and D was calculated.

Fraenknel and Wouben (11) determined the diffusivity of gold in silver by etching resistance technique. Etching reagents under certain circumstances no longer attack solid solutions, if a certain percentage of the nobler metal is exceeded. Thus they found out the depth and concentration of gold in silver after diffusion anneal, and hence diffusivity was calculated.

These methods can be applied only for a few special cases. Beside their accuracies are also limited. For exact measurement it is advisable to determine the course of concentration along the diffusion path by means of quantitative analysis.

One way to perform this is to bring into contact two cylinders of different metals. The couple can now be annealed and fine chips can then be turned off, measuring every time the depth. The chips are now analysed and c-x (concentration - distance) curves are plotted. The difficulty with this method is that only a very limited quantity of metal is available for chemical analysis. Moreover, it is difficult to fix two cylinders such that the original boundary plane is perpendicular to the axis of rotation. Quicker and better method of analysis like emission-spectrography, etc., can be used to a big advantage. From the c-x plot the diffusivity can be obtained from equation (3.7) using Gauss error function table. It must be mentioned that

the solution of Fick's second law here is under semi-infinite assumption and hence diffusion should not be allowed to such an extent that boundary conditions are altered.

(ii) Physical methods

The physical methods used for diffusivity measurement are limited in number and can be used for very special cases. These consist of measuring conductivity or determining lattice spacing and relating them to the concentration of solute.

(iii) Tracer methods

The determination of diffusivity in general involves two steps. After diffusion anneal we must be able to determine the concentration and distance of that layer from interface. These can be most easily achieved by use of tracers because concentration and depth of penetration can be related to emitted radiation. There are in general seven ways of measuring diffusivity by tracers.

The first method that was developed is called "The Sample Sectioning Method." A couple of natural and radioactive metal is first annealed. Very thin layers parallel to the interface are then removed and their activity is measured. The distance of the layer removed from the interface is noted and measured activity is related to concentration. Thus we get the c-x curve and hence diffusivity.

The difficulty with this method is that it is very difficult to remove such thin layers. If diffusivity is very low which is generally true for metals, the distance till which activity of removed layers that can be measured is also small and measurements never become inaccurate.

The basis of the second method known as absorption technique was developed by Nix (43). The method is based on the fact that radiation is absorbed by base metal. Hence if we know the absorption co-efficient, we can determine the depth to which tracers have moved and their relative concentration by measurement of activity. The theory needs application of Beer's and Lambert's laws of absorption. This method required the necessary pre-knowledge of absorption characteristics, also validity of Beer's and Lambert's law can be questioned for intensities of radioactive radiation.

In the third method a quadrangular sample is covered by isotope. After annealing, the distribution of activity in a plane perpendicular to the edge (the layer of isotopes) indicates the nature of distribution of tracers and thus gives the diffusivity. This method requires a very precise counting technique.

The fourth method consists of coating one side of a thin sample (22) with a radioactive isotope and measuring the intensities of radiation on both sides as a function of annealing time. The slope of the plot of $\ln(I_1-I_2/I_1+I_2)$-t gives us the diffusivity, as

$$\ln \frac{I_1 - I_2}{I_1 I_2} = \ln K - \frac{\pi^2 D}{l^2} t \qquad (3.23)$$

Where I_1, I_2 = activities at time t on coated and uncoated side respectively,

l = thickness of the sample,

K = constant.

The equation (3.23) is obtained from solution of Fick's second law, which is expressed as

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

Under the boundary conditions, that at $t = o$

$c = c_o$ when $o \leqslant x < h$

$c = 0$ when $h < x \leqslant l$

where h is the thickness of coating.

The solution turns out to be (22)

$$C = C_0 \left(\frac{h}{l} + \frac{2}{\pi} \sum_{1}^{\infty} \frac{1}{n} \exp\left[- \left(\frac{\pi n}{l}\right)^2 Dt\right] \quad \text{Cos} \frac{n\pi x}{l} \text{ Sin} \frac{n\pi h}{l}\right) \qquad (3.24)$$

The series converges very rapidly and hence for a long annealing time it is possible to write

$$C = C_0 \left(\frac{h}{l} + \frac{2}{\pi} \exp\left[- \left(\frac{\pi}{l}\right)^2 Dt\right] \quad \text{Cos} \frac{\pi x}{l} \text{ Sin} \frac{\pi h}{l}\right) \qquad (3.25)$$

and for $h \ll 1$, we get

$$C = C_0 \frac{h}{1} \left(1 + 2 \exp\left[-\left(\frac{\pi}{1}\right)^2 Dt\right] \cdot \operatorname{Cos} \frac{\pi x}{1}\right) \qquad (3.26)$$

If dI is the radiation at one side through a thickness dx of the sample, then

$$\int_0^{I_1} dI_1 = \int_0^{l} c_x B \, f\,(x,\, 1-x)\, dx \qquad (3.27)$$

Where B = number of impulses radiated from a unit volume

$f(1,1-x)$ = a function that takes account of absorption.

Integrating equation (3.27) we get

$$I_1 = \int_0^{1} C_x \, B \, f\,(x,\, 1-x)\, dx \qquad (3.27a)$$

Similarly

$$I_2 = \int_0^{1} C_x \, B \, f\,(1-x,\, x)\, dx \qquad (3.27b)$$

Integrating by parts the equation (3.27a) and (3.27b) we obtain

$$\frac{I_1}{I_2} = \frac{\int_0^{l} f\,(x,1-x)\, dx + 2\exp(-mt) \int_0^{l} \operatorname{Cos} \frac{\pi x}{1} f\,(x,1-x)\, dx}{\int_0^{1} f\,(1-x,x)\, dx + 2\exp(-mt) \int_0^{1} \operatorname{Cos} \frac{\pi x}{\pi 1} f\,(1-x,x)\, dx} \qquad (3.28)$$

$$\frac{I_1}{I_2} = \frac{1 + k \exp(-mt)}{1 - k \exp(-mt)} \qquad (3.29)$$

Where

$$m = \frac{\pi^2 D}{l^2} \tag{3.29a}$$

$$k = \frac{2 \int_0^l \text{Cos} \frac{\pi x}{l} f(x, l-x)\, dx}{\int_0^l f(x, l-x)\, dx} \tag{3.29b}$$

and from equation (3.29) we obtain equation (3.23), i.e.,

$$\ln \frac{I_1 - I_2}{I_1 + I_2} = \ln k - mt$$

Thus we can determine D by measurement of I_1 and I_2 as a function of annealing time.

The method outlined is simple and quick. It has a good possibility to be used at low temperature. A small number of samples can be used. There are no laborious and difficult sectionings to be done. The most important advantage is that it is not necessary to know about the absorption coefficient, because the absorption part is separated as the constant K.

The fifth method known as thick layer method (50) was developed by Geodaykyan and Zhoukhovitzky. Here a thick sample is coated with a tracer on one side and is enclosed in a lead box with a lid. The lid is placed on the uncoated side. The activity is measured once after removing the lid

and once when it is partially open. From the plot of the ratio between activities and $1/\sqrt{t}$ the diffusivity can be determined.

The sixth method called the oblique cut method was introduced by Ahmed Azzam and Nach Gatos (2). Here a cylindrical couple after annealing is cut obliquely and symmetrically across the interface. The cut plane is then exposed in front of a photographic film. A plot is then made of darkening of film versus distance and diffusivity is found from this. The plane along which the cut is made must make a known angle and must not deviate at any position. This brings in complication.

In the seventh or residual activity technique, the decrease of surface concentration on the coated side is measured after each anneal. The surface activity then can be related to D and annealing time and hence D can be calculated. This is a very fast method and has no complication of measurement. But surface diffusion, if it occurs in a long extent, can give erroneous result.

These are in general the different methods available for measurement of diffusivity. The merit of each process depends on the metal to be studied.

IV. EXPERIMENT

The method chosen for measurement of diffusivity of Cu^{64} in mild steel was the thin layer technique (22). This method was chosen because it is easy to get a thin sample of mild steel, Cu^{64} can be easily plated on steel and the diffusion in Fe does not change due to the thinness of sample (22).

The basic steps of the experiment were as follows. A thin mild steel sheet was cut to 1 cm x 1 cm. It was then polished and coated with Cu^{64} on one side. This was heated to the required temperature under 10^{-5} mm. Hg vacuum. Every half hour it was taken out and activity of each side was measured by a counter.

1. Apparatus

A line sketch of the apparatus is shown in Fig. 1. The apparatus consists of

1. Tube furnace (C)
2. Heating tube (A)
3. Tube joint (B)
4. McLeod pressure gauge (D)
5. Mechanical pump (E)
6. Diffusion pump (F)
7. Thermocouple and thermostat

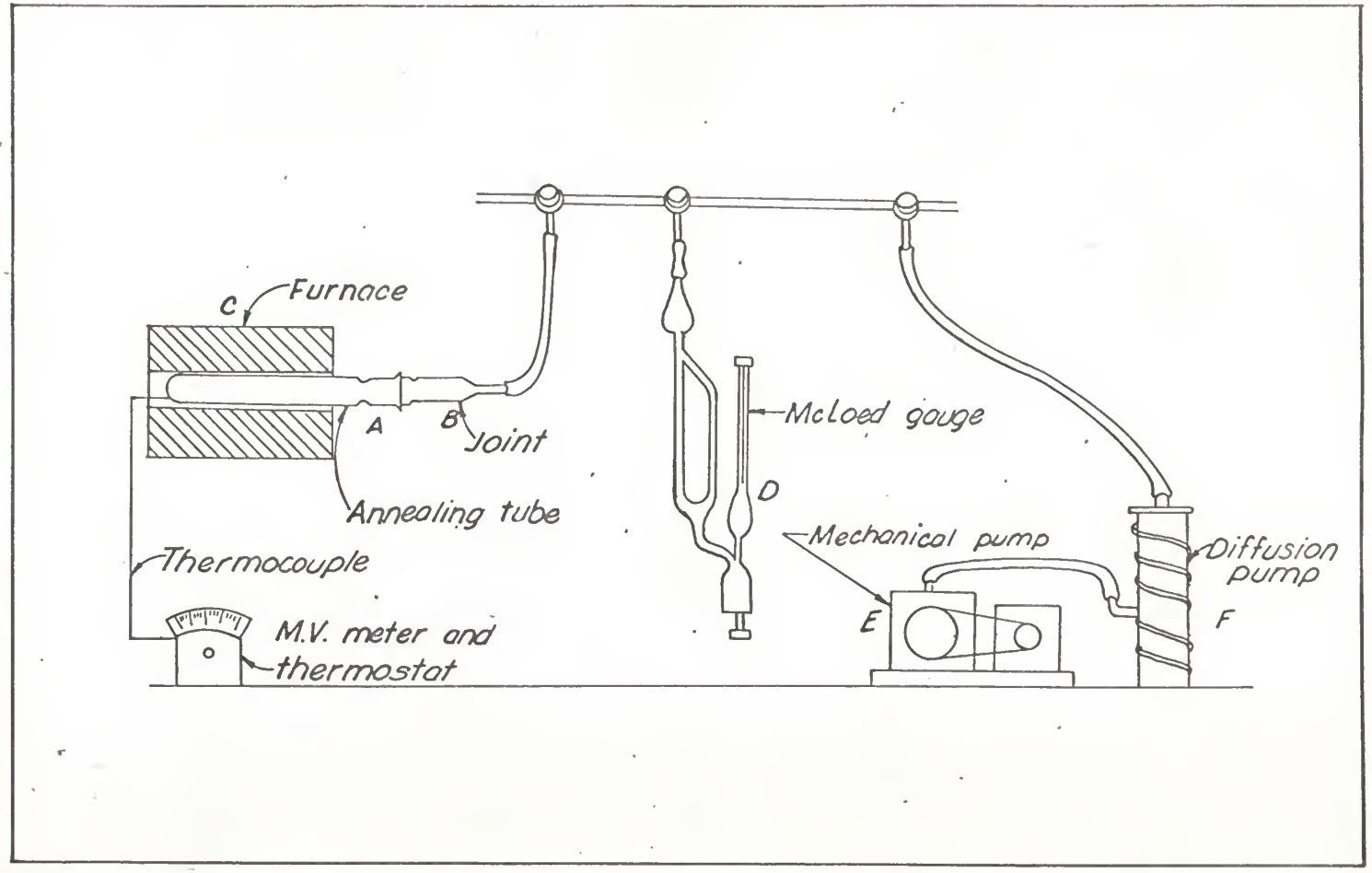

Fig. 1. Line sketch of the apparatus

The resistance furnace (C) used, gave temperature up to 1000°c. The annealing tube (A) was made of Vycor glass whose softening temperature is 1200°c. The McLeod pressure gauge was capable to measure pressure up to 10^{-5} mm. Hg. The vacuum was produced by mechanical and diffusion pump. The diffusion oil was of silicone base which resists decomposition and has special affinity for oxygen. Chrome-alumel thermocouple was used for recording temperature. It was calibrated with a standard. The thermocouple was coupled to a thermostat. The accuracy of temperature measurement was $\pm$ 1.5°c.

2. Preparation of sample

The sample was cut off from a .01 mm thick mild steel sheet. The sample was checked for evenness by measuring thickness at various points. The sample was then polished on both sides to 600 fineness taking care that no scratch was present.

The tracer used in this study was Cu^{64} isotope. This isotope has a half life of 12.9 hours with 40% β and 60% γ radiation. About .06 g of natural Cu powder was activated to .05 m Cu. The natural Cu was 99.95% pure. The γ ray spectrum was checked to detect if any long half life impurity was present and gave a satisfactory result. The activated Cu^{64} was dissolved in 2ml of concentrated H_2SO_4 by boiling. The solution was then diluted ten times. The

polished samples were kept on a filter paper moistened by the solution, for 45 seconds. This guarnteed coating of Cu^{64} was on one side of the samples. The samples were then washed with soap solution and then with acetone. The coating was about .02 μ. The thickness was measured by weighing before and after plating.

3. Annealing and activity measurement

The sample was first put into tube B after the tube A was heated to the required temperature. The system was then closed and evacuated up to 10^{-5} mm Hg. The furnace was then tilted to drop the sample in tube A. Every half hour the sample was again brought in tube B by tilting the furnace. Then the sample was taken out from tube A by the same way in order to measure the activity of both sides by a scalor counter fitted with an Anthracin crystal to filter off the γ rays. The measuring probe was enclosed in a lead chamber to minimise the background. The high voltage used was to give maximum sensitivity. Counting was done five times for one minute each on both sides.

4. Sources of errors

There are three sources of expected error

(i) Activity measurement

(ii) Temperature measurement

(iii) Geometric measurement

Among these the first two are the main sources of error. The error due to activity measurement is given by (22).

$$\gamma_D = \frac{2}{I_1 - I_2} \cdot \frac{1}{\ln\left[\frac{I_1^o - I_2^o}{I_1^o + I_2^o}\right]} \qquad (5.1)$$

where

γ_D = error in diffusivity

I_1^o, I_2^o = initial activities on coated and uncoted side respectively.

Since the measured activities were more than 10^6 the maximum expected errors will be

$$\gamma_D = \frac{2}{10^3} \times \frac{1}{1.2} = 1.7 \times 10\text{-}3$$

or

$$\gamma_D = \pm 0.8\%$$

The error due to temperature measurement is given by (22)

$$\gamma_D = \frac{Q}{RT} \gamma_T$$

where γ_T is inaccuracy in temperature. The inaccuracy in temperature was $\pm$ 1.5° and hence maximum error will be

$$D = \pm \frac{47,000}{2x600} \times \frac{1.5}{600} \times 100$$

or

$$D = \pm 10\%$$

The geometric errors consist of errors in measurement of thickness and inaccuracy due to the position of the sample during activity measurement. The later error can be minimized if the sample is placed near to the probe (22). Total error d e to geometric factors may be estimated to be about 3%.

The total error due to all sources then should not exceed $\pm$ 12%.

V. RESULTS AND DISCUSSION

In thin layer technique the activities (I_1, I_2) and annealing time is related by the equation (3.23), which is

$$\ln \frac{I_1-I_2}{I_1+I_2} = K - \frac{\pi^2 D}{l^2} t$$

The plots between ln (I_1-I_2/I_1+I_2) and t are straight lines. These are known as kinetic curves. In Fig. 2, 3 and 4, the kinetic curves obtained for α, $\alpha+\gamma$ and γ phase respectively are presented. The slopes of these lines were calculated by least square technique. The computor output and program is presented in the appendix. The slope of the kinetic curves yield the diffusivities at various annealing temperatures. The measured diffusivities are presented in Table 1.

The plots between log D and 1/T are shown in Fig. 5. These gave straight lines, which confirm that Arrhenius equation (3.18) is applicable in these cases. The activation energy (Q) and frequency factors (D_0) were calculated from Arrhenius plots. They are presented in Table 2.

The diffusivity (D*) of Cu in pure Fe was reported (40) to have an activation energy of 61,000 Cal and frequency factor of 3. The activation energy measured in this work for diffusion of Cu^{64} in mild steel below transformation point was 47,000 Cal. This shows a definite decrease in the value

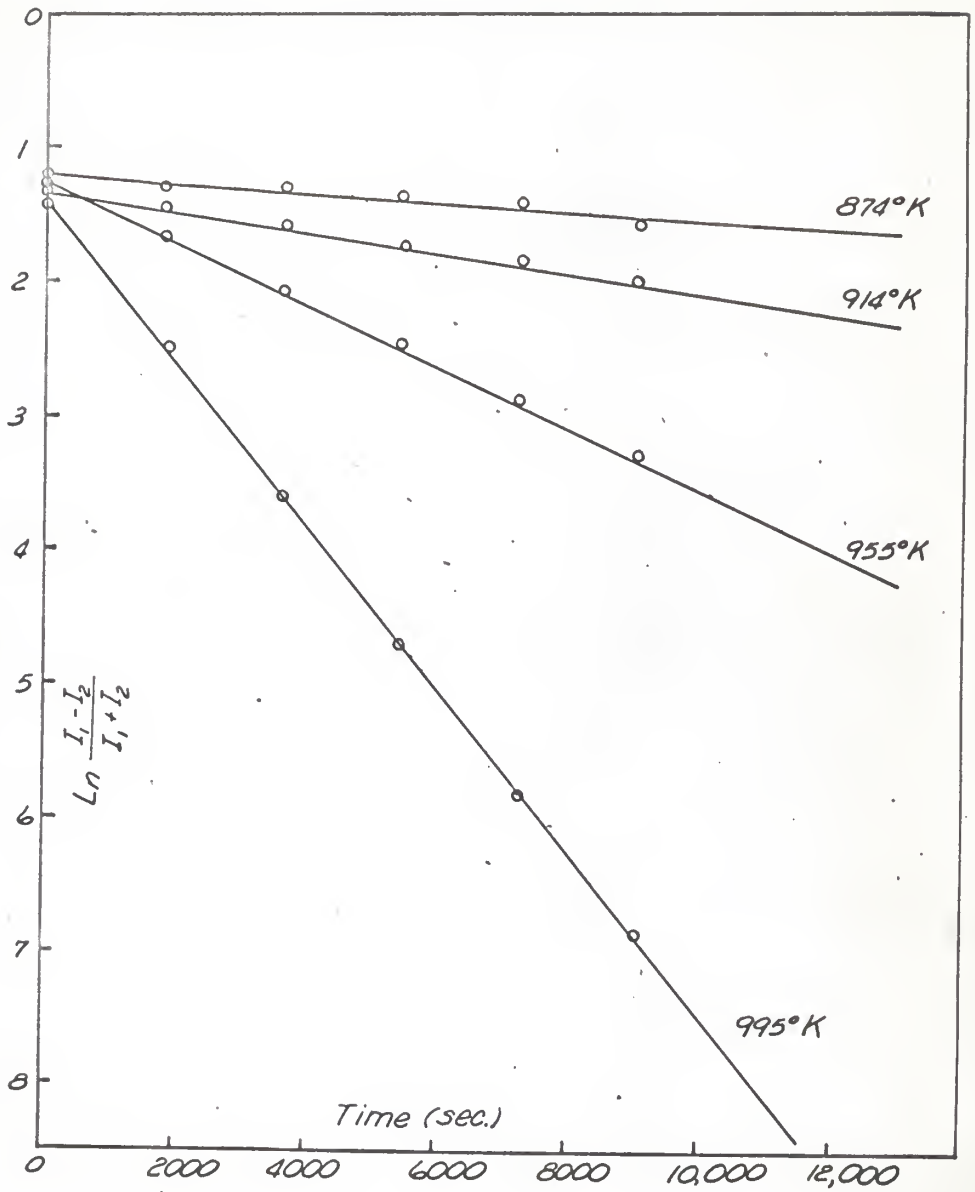

Fig.2. Kinetic curve for α Fe

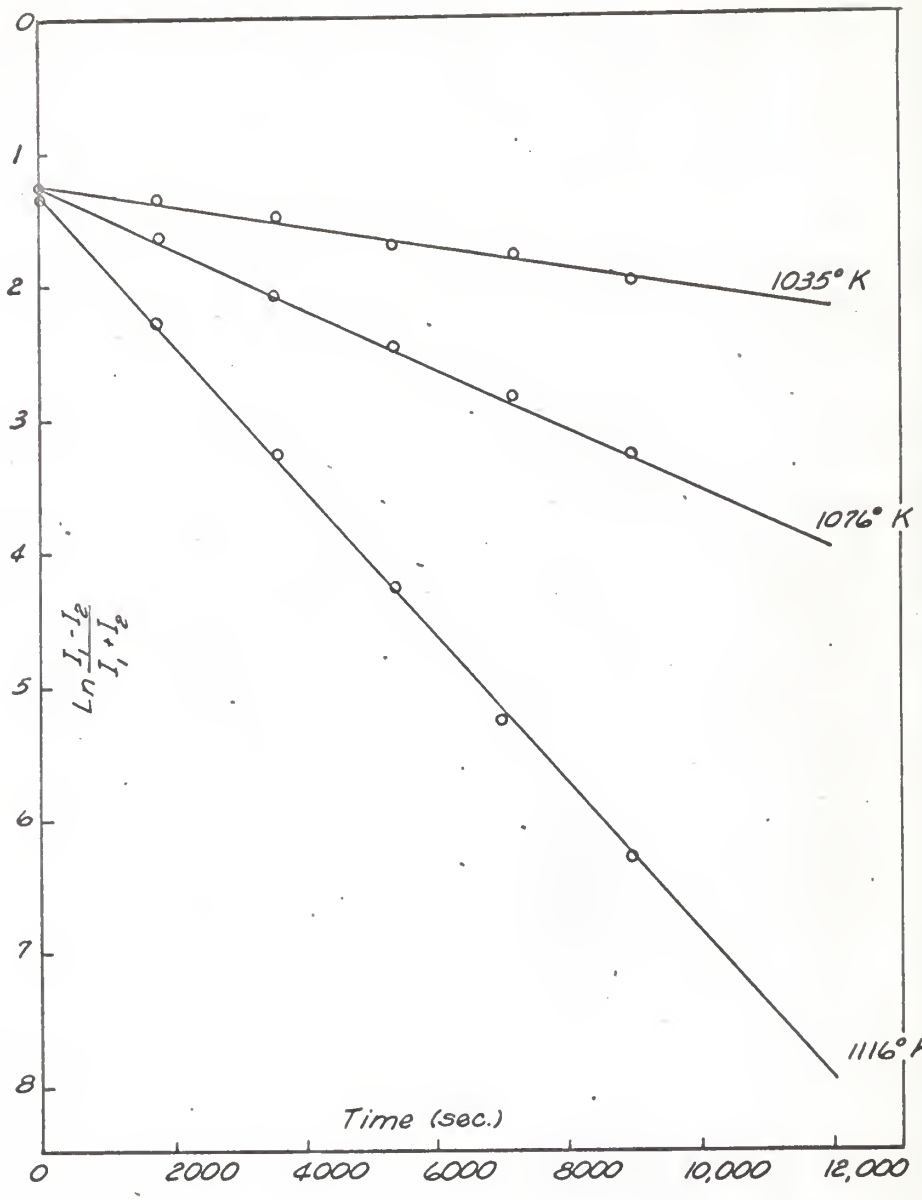

Fig.3. Kinetic curve for $\alpha + \gamma$ Fe

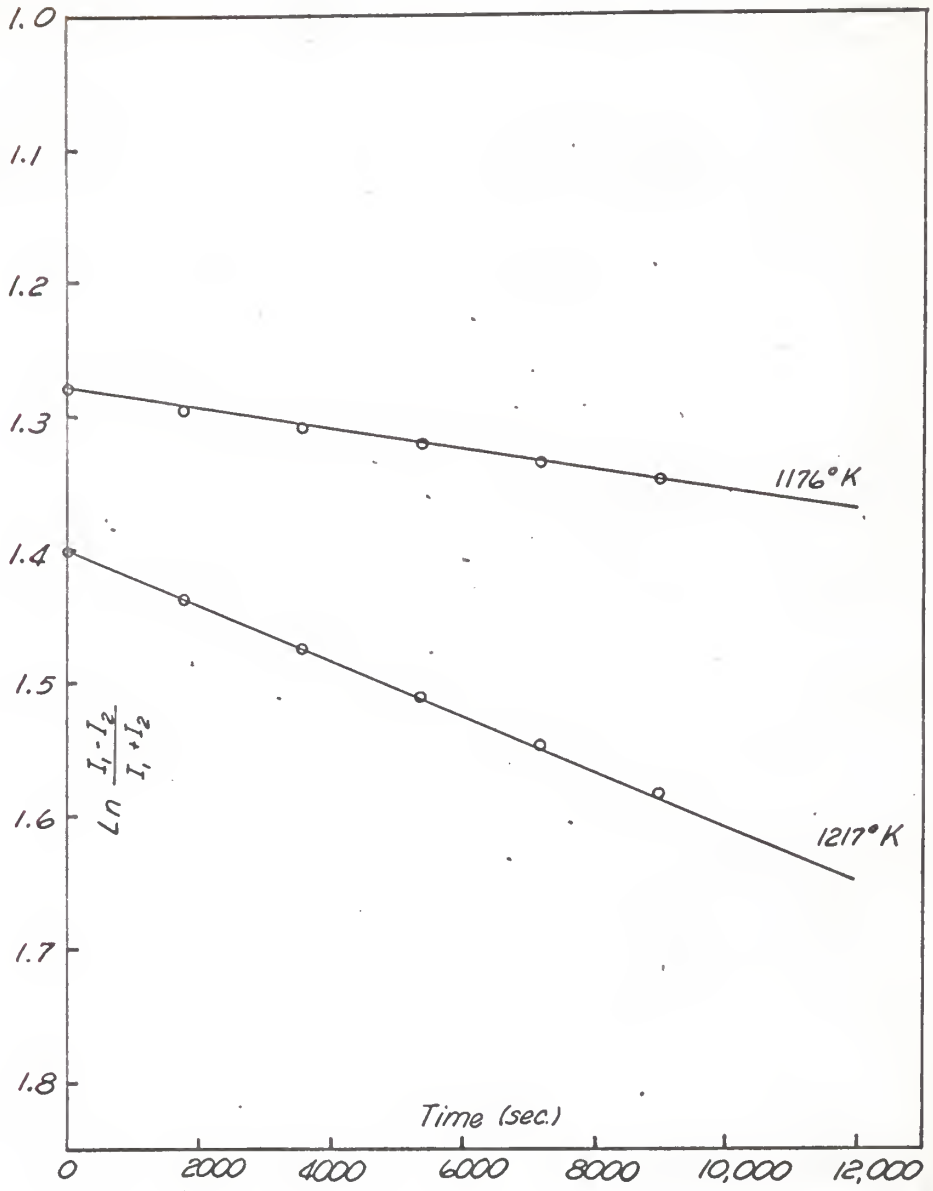

Fig. 4. Kinetic curve for γ Fe

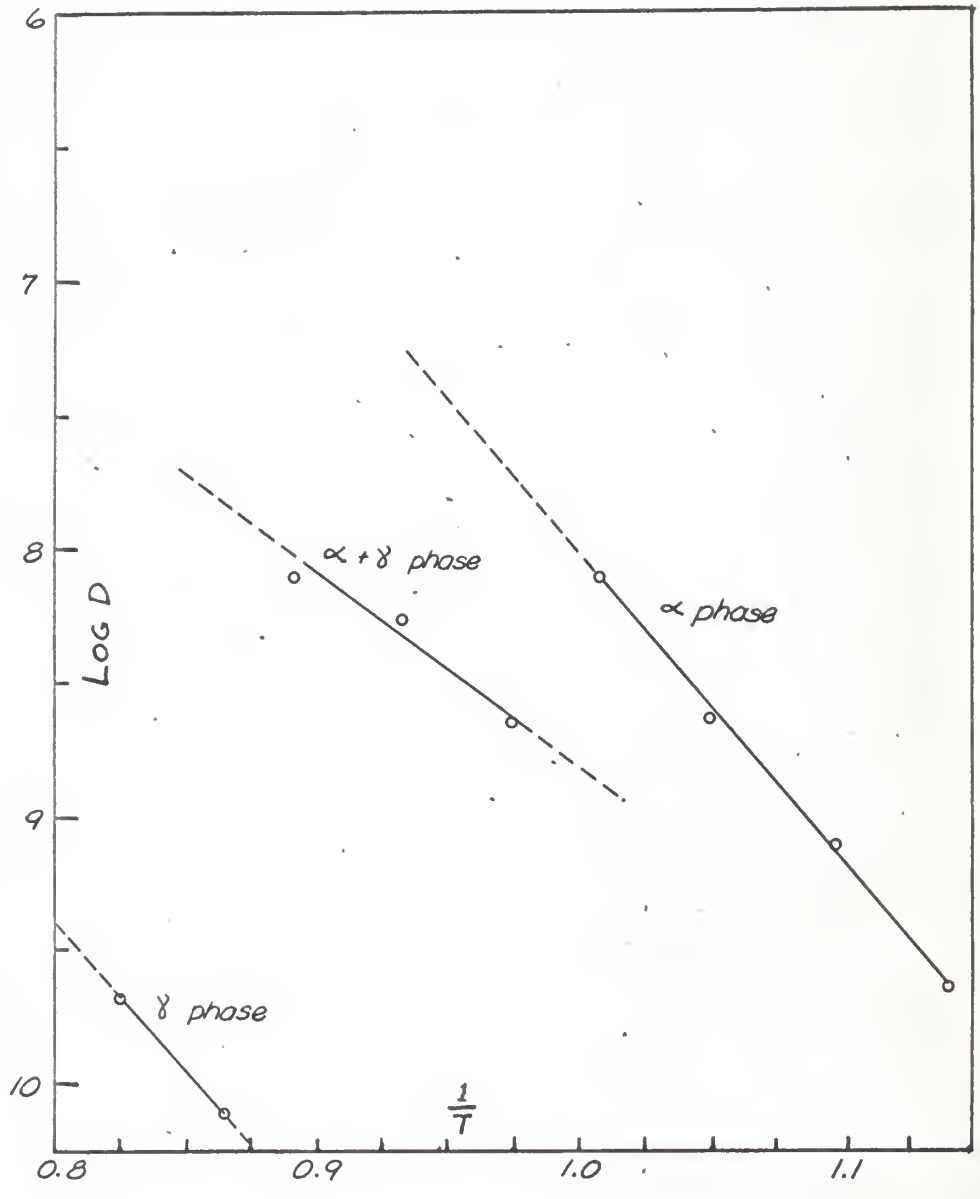

Fig. 5. Arhenius plot

Table 1. Diffusivities at different temperatures.

No.	Phase	Temperature ^{o}K	Diffusivity $Cm^2/Sec.$
1.	α	874	2.3×10^{-10}
2.	α	914	7.6×10^{-10}
3.	δ	955	2.3×10^{-9}
4.	α	995	6.2×10^{-9}
5.	$\alpha + \gamma$	1035	7.6×10^{-10}
6.	$\alpha + \gamma$	1076	2.3×10^{-9}
7.	$\alpha + \gamma$	1116	5.6×10^{-9}
8.	γ	1176	7.6×10^{-11}
9.	γ	1217	2.1×10^{-10}

Table 2. Frequency factors and activation energies for different phases

No.	Phase	Frequency factor cm^2/Sec	Activation energy Cal/gm mole
1	α	134	47,000
2	$\alpha+\gamma$	729	57,000
3	γ	591	70,000

of activation energy. This may be due to intersticial carbon atoms dissolved in body centered cubic matrix.

The interstitial atoms increase the lattice constant. In other words, they tend to push the Fe atoms apart and hence it takes less energy to form a vacancy. The activation energy as described by equation (3.18b) is the sum of energy required for vacancy formation (Q_f) and energy required for a jump of Cu^{64} atom (Q_m) in that vacancy, per gm. mole of substance. The value of Q_f decreases due to the presence of interstitial impurities. But due to the presence of the carbon atom, more energy should be necessary for jump of Cu^{64} atom, i.e., Q_m should increase. The decrease in activation energy in case of mild steel shows that Q_f is affected more than Q_m. This effect can be better understood if further work is done with different amount of carbon in steel.

It may be observed from Table 2 that the activation energy increases to 57,000 Cal in $\alpha+\gamma$ range and to 70,000 in austenite. This may be due to the presence of excessive dislocations. The maximum carbon that can dissolve in α-iron is .025%, but austenite can dissolve all the carbon present in mild steel. It is true that this should have stronger effect on Q_f than below transformation point, but the number of dislocations present also increases with amount of impurities present. The dislocations deviate from the regular arrangement of atoms and a strain field exists around them. They are prone to release this strain by absorbing

vacancies and if the effect sue to number of dislocations exceed the effect of lattice deformation by presence of impurities, then activation energy should increase. It seems that in case of mild steel in austenite form, this effect might have occurred.

The frequency factor for diffusion of Cu in Fe was reported (40) to be 3. The frequency factors measured in this work were much greater than the reported value. It was shown in equation (3.18a) that the frequency factor is an exponential function of entropy of the lattice. For the same reasons discussed in the previous paragraph, the increase in frequency factor may be due to increase in lattice entropy resulted from the strains induced by the presence of impurities and dislocations.

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APPENDIX

```
* LIST OF SYMBOLS USED IN THE COMPUTER PROGRAME *
A=I(1)
B=I(2)
M= NUMBER OF SETS
N= NUMBER OF READING PER SET


C  C CALCULATION OF DIFFUSIVITY BY LEAST SQUARE METHOD
      DIMENSIONA(10),B(10),C(10),D(10),X(10),Y(10)
      DIMENSION S(9),R(9),TEMP(10),TIME(10)
  100 FORMAT(F7.2,F7.2,F7.2)
  102 FORMAT(I5,I5)
  101 FORMAT (14HDIFFUSIVITY AT F5.0,7HKELVIN=E15.2)
  103 FORMAT(18HACTIVATION ENERGY=E10.2)
  104 FORMAT(17HFREQUENCY FACTOR=F10.2)
      AA=0.
      SL=0
      P=1
      Q=0
      READ 102,N,M
      DO 2 J=1,M
      DO 1 I=1,N
      READ 100,A(I),B(I),TIME(I)
      Y(I)=LOG((A(I)-B(I))/(A(I)+B(I)))
      X(I)=TIME(I)
      S(I)=A(I)+B(I)
      R(I)=A(I)-B(I)
      PUNCH 105,TIME(I),A(I),B(I),S(I),R(I),Y(I)
  105 FORMAT(F6.1,4X,F6.1,4X,F6.1,4X,F6.1,4X,F6.1,4X,F6.3)
    1 CONTINUE
      AA=N
      CALL SLOPE
      D(J)=-1.*((SL*0.0001)/(3.14**2))
      ABS=0
      ORD=0
      READ 100,TEMP(J)
      TEMP(J)=TEMP(J)+273.
    2 PUNCH 101,TEMP(J),D(J)
      DO 3 I=1,M
      Y(I)=LOG(D(I))
      X(I)=1./TEMP(I)
    3 CONTINUE
      N=M
      AA=M
      CALL SLOPE
      Q=ORD/AA-SL*ABS/AA
      E=-SL*2.
      P=EXP(Q)
```

```
      PUNCH 103,E
      PUNCH 104,P
      GO TO 10
      SUBROUTINE SLOPE
      PROD=0.
   40 SQ=0.
   50 ABS=0
      ORD=0.
      DO 6 I=1,N
      ABS=ABS+X(I)
    6 ORD=ORD+Y(I)
      DO 4 I=1,N
      PROD=PROD+(ABS/AA-X(I))*(ORD/AA-Y(I))
    4 SQ=SQ+(ABS/AA-X(I))**2
      SL=PROD/SQ
      RETURN
   10 STOP
      END
```

* DIFFUSIVITIES BELOW TRANSFORMATION POINT *

(1)	(2)	(3)	(4)	(5)	(6)
TIME	I(1)	I(2)	I(1)+I(2)	I(1)-I(2)	LN((5)/(4))
.0	287.7	154.5	442.2	133.2	-1.200
1800.0	268.2	147.9	416.1	120.3	-1.241
3600.0	243.7	137.7	381.4	105.9	-1.281
5400.0	232.1	134.4	366.5	97.7	-1.322
7200.0	214.9	127.2	342.1	87.6	-1.362
9000.0	202.3	122.4	324.7	79.9	-1.403
DIFFUSIVITY AT 874.KELVIN=			0.23E-09		
.0	76.5	43.8	120.3	32.8	-1.300
1800.0	69.0	42.4	111.4	26.5	-1.434
3600.0	62.3	40.9	103.2	21.5	-1.570
5400.0	60.1	41.6	101.7	18.5	-1.703
7200.0	52.9	38.4	91.2	14.5	-1.839
9000.0	50.4	38.1	88.4	12.3	-1.972
DIFFUSIVITY AT 914.KELVIN=			0.76E-09		
.0	662.2	367.2	1029.4	294.9	-1.250
1800.0	589.1	400.0	989.1	189.1	-1.654
3600.0	531.2	411.0	942.2	120.3	-2.059
5400.0	484.8	408.6	893.4	76.1	-2.463
7200.0	457.3	408.1	865.3	49.2	-2.867
9000.0	428.2	396.9	825.1	31.3	-3.271
DIFFUSIVITY AT 955.KELVIN=			0.23E-08		
.0	146.5	88.6	235.1	58.0	-1.400
1800.0	124.3	105.5	229.8	18.9	-2.499
3600.0	114.6	108.5	223.1	6.1	-3.599
5400.0	97.5	95.7	193.2	1.8	-4.698
7200.0	97.4	96.8	194.2	.6	-5.780
9000.0	88.8	88.6	177.4	.2	-6.893
DIFFUSIVITY AT 995.KELVIN=			0.62E-08		

ACTIVATION ENERGY= 0.47E+05

FREQUENCY FACTOR= 134.60

* DIFFUSIVITIES DURING TRANSFORMATION

(1)	(2)	(3)	(4)	(5)	(6)
TIME	I(1)	I(2)	I(1)+I(2)	I(1)-I(2)	LN((5)/(4))
.0	49[illegible].0	27[illegible].1	76[illegible].1	22[illegible].0	-1.240
1800.0	455.[illegible]	271.3	726.2	183.7	-1.375
3600.0	421.7	269.[illegible]	69[illegible].7	152.7	-1.509
5400.0	392.9	265.6	658.5	127.3	-1.644
7200.0	363.1	258.2	621.3	105.0	-1.778
9000.0	338.8	251.6	590.4	87.2	-1.913
DIFFUSIVITY AT1[illegible]35.KELVIN=			[illegible].76E-09		
.0	1025.1	565.0	159[illegible].1	460.1	-1.240
1800.0	923.6	624.6	1548.2	299.0	-1.644
3600.0	844.6	651.7	1496.3	192.9	-2.049
5400.0	795.2	669.2	1464.3	126.0	-2.453
7200.0	731.3	651.8	1383.1	79.4	-2.857
9000.0	704.8	652.8	1357.6	52.0	-3.261
DIFFUSIVITY AT1076.KELVIN=			[illegible].23E-08		
.0	747.0	427.1	1174.1	320.0	-1.300
1800.0	618.8	505.5	1124.3	113.4	-2.294
3600.0	556.3	516.3	1072.5	40.0	-3.289
5400.0	531.4	517.0	1048.4	14.5	-4.284
7200.0	489.2	484.3	973.5	5.0	-5.275
9000.0	461.3	459.5	920.8	1.7	-6.271
DIFFUSIVITY AT1116.KELVIN=			0.56E-08		

ACTIVATION ENERGY= 0.57E+05

FREQUENCY FACTOR= 729.10

* DIFFUSIVITIES IN AUSTENITE *

(1)	(2)	(3)	(4)	(5)	(6)
TIME	I(1)	I(2)	I(1)+I(2)	I(1)-I(2)	LN((5)/(4))
.0	1190.0	672.2	1862.2	517.8	-1.280
1800.0	1138.2	648.2	1786.3	490.0	-1.293
3600.0	1088.6	624.9	1713.5	463.7	-1.307
5400.0	1039.7	601.5	1641.2	438.2	-1.320
7200.0	976.5	569.3	1545.8	407.2	-1.334
9000.0	932.5	547.8	1480.2	384.7	-1.347
DIFFUSIVITY AT1176.KELVIN=			0.76E-10		
.0	550.0	332.4	882.4	217.6	-1.400
1800.0	507.8	312.7	820.5	195.0	-1.437
3600.0	481.3	301.8	783.1	179.5	-1.473
5400.0	469.0	299.3	768.3	169.7	-1.510
7200.0	460.6	298.8	759.4	161.7	-1.547
9000.0	444.9	293.3	738.2	151.5	-1.583
DIFFUSIVITY AT1217.KELVIN=			0.21E-09		

ACTIVATION ENERGY= 0.70E+05

FREQUENCY FACTOR= 591.42

MEASUREMENT OF DIFFUSIVITY OF Cu^{64} IN MILD STEEL BY THIN LAYER TRACER TECHNIQUE

by

SAIBAL GANGULY

B. S. (Met. Eng.) Indian Institute of Technology,
Bombay, India, 1966

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Industrial Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1968

This report presents the results of an investigation done on the effect of interstitial impurities on diffusion of copper-64 in iron. The thin layer tracer technique was used for measurements of diffusion coefficient in the temperature range of 600°C. to 940°C. The diffusivities, which followed Arrhenius relation are:

$D = 134 \exp(-47{,}000/RT)$ below transformation point,

$D = 729 \exp(-57{,}000/RT)$ during transformation,

and

$D = 591 \exp(-70{,}000/RT)$ in austenite.

The changes in activation energies and frequency factors may be due to the phase changes and increased strain in lattice for the presence of interstitial impurities. The increase in the energy values in austenite and during transformation may be due to the presence of more dislocations which absorb the vacancies.